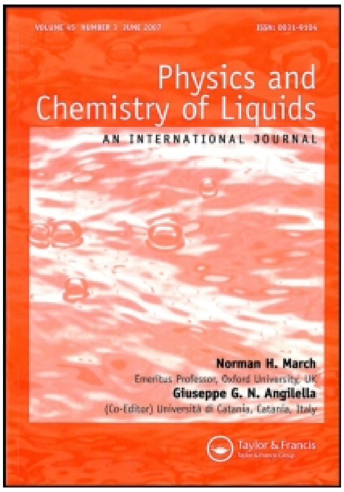

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Determination of Stability Constants of Charge Transfer Complexes of CycloAlkanones with Tetrachloroethylene in n -Hexane Solutions by Ultrasonic Method

V. Kannappan[a]; R. Jaya Santhi[a]; S. Xavier Jesu Raja[b]
[a] Post Graduate and Research Department of Chemistry, Presidency College, Chennai, India [b] Department of Physics, Loyola College, Chennai

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DETERMINATION OF STABILITY CONSTANTS OF CHARGE TRANSFER COMPLEXES OF CYCLOALKANONES WITH TETRACHLOROETHYLENE IN *n*-HEXANE SOLUTIONS BY ULTRASONIC METHOD

V. KANNAPPAN[a,]*, R. JAYA SANTHI[a] and S. XAVIER JESU RAJA[b]

[a]*Post Graduate and Research Department of Chemistry, Presidency College, Chennai – 600 005, India;* [b]*Department of Physics, Loyola College, Chennai – 600 034*

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The ultrasonic velocity (U), density (ρ) and viscosity (η) of solutions containing equimolar concentration of four cycloalkanones (cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone) and Tetrachloroethylene (TCE) in n-hexane solutions have been measured at five different temperatures in the range 293–313 K. Acoustical parameters such as adiabatic compressibility (β), Rao constant (R), absorption coefficient (α/f^2), free energy of activation (ΔG^*), internal pressure (π_i), cohesive energy (CE), free volume (V_f), molecular interaction parameter with respect to ultrasonic velocity (X_u), density (X_ρ), and viscosity (X_η) were calculated from the experimental data. Formation constant (K) values of the charge transfer (CT) complexes have been evaluated using a modified Bhat equation. Thermodynamic parameters such as free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) for the formation of these complexes are computed from the variation of formation constant values with temperature. The stability constants of the charge transfer complexes formed between four cyclicketones and TCE correlate satisfactorily with polarisability (α), and ionization potential (IP) values of the ketones.

Keywords: Ultrasonic velocity; Charge transfer complexes; Cycloalkanones; Tetrachloroethylene

1. INTRODUCTION

Carbonyl group is a polar group and aldehydes and ketones containing this group act as π and n electron donors. They can form donor–acceptor complexes with compounds like chloroform through intermolecular hydrogen bond [1,2] or with electron deficient molecule through dipole–dipole interaction. The formation of such complexes between chloroform and aliphatic ketones has been detected by spectral method [3,4]. In this laboratory, ultrasonic studies have been carried out to detect charge transfer complexes between ketones and chloroform and the stability constants of these complexes were calculated using a modified Bhat equation [2]. These stability constants correlate

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*Corresponding author.

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satisfactorily with the total charge density on the carbonyl oxygen of the ketones. Tetrachloroethylene (TCE) is an electron deficient molecule due to the presence of electron withdrawing chloro substituent. It can act as an electrophile. In this article we report the results obtained on the study of molecular interaction between four cyclicketones namely, cyclopentanone, cyclohexanone, cycloheptanone, and cyclooctanone in the temperature range 293–313 K. Acoustical parameters such as adiabatic compressibility (β), Rao constant (R), absorption coefficient (α/f^2), free energy of activation (ΔG^*), internal pressure (π_i), cohesive energy (CE), molecular interaction parameter with respect to ultrasonic velocity (X_u), density (X_ρ), and viscosity (X_η) are also reported in this article. The thermodynamic parameters such as free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) are determined from the stability constant values at different temperatures.

2. EXPERIMENTAL

Cyclicketones such as cyclopentanone, cyclohexanone, cycloheptanone, and cyclooctanone are used as electron donor and TCE is used as an electron acceptor. These compounds are of the Laboratory Reagent grade samples, which were purified by the standard methods as described in the Literature [5,6] before use. The boiling points of these liquids agree with the literature values [2] suggesting that the liquids in the present study are of ultra purity. All the test solutions were prepared and stored in airtight amber bottles to minimize the absorption of moisture. Solutions containing equimolar quantities of cyclicketones and tetrachloroethylene in *n*-hexane were prepared fresh and thermostated before determining ultrasonic velocity, density, and viscosity measurements.

The ultrasonic velocities of pure liquids and their mixtures were measured using multifrequency ultrasonic interferometer at 2 MHz (MITTAL ENTERPRISES New Delhi, Model F-81). Viscosities of pure compounds and their liquid mixtures were determined in an Oswald's viscometer calibrated with double-distilled water. The viscometer containing the test liquids was allowed to stand for about 15 min in the thermostatic water bath to minimize thermal fluctuation of the viscometer. Densities of pure components and their solutions were measured accurately using 10 mL specific gravity bottles in an electronic balance precisely within ± 0.1 mg accuracy. The temperature of the test solutions and their mixtures were maintained to an accuracy of ±0.01°C. The accuracy in the measurement of density and viscosity of the liquids are of the order of ±1 part in 10^3 parts and 0.1% respectively.

The ultrasonic velocities, densities, and viscosities were determined at 293, 298, 303, 308 and 313 K respectively.

3. COMPUTATIONAL METHODS

Intermolecular free length, Rao constant, absorption coefficient, free volume, cohesive energy, free energy of activation, and the molecular interaction parameters were calculated from the ultrasonic velocity, density, and viscosity values using standard equations [7–10]. To calculate the stability constants of donor–acceptor complexes in binary liquid mixture, Marwein and Bhat [11] have proposed an equation. Their equation gives formation constant values in binary liquid mixtures which is concentration dependent and can be applied in moderate concentration. In our earlier paper [2] we have given a new modified Bhat equation to calculate the formation constant values of the charge transfer complexes, applicable to weak complexes even in very dilute solution.

4. RESULTS AND DISCUSSION

Aldehydes and ketones can form charge transfer complexes with the acceptor molecules through electron deficient sites. It has been found that the carbonyl compounds form charge transfer complexes with chloroform through intermolecular hydrogen bond [1,2]. The formation constants of these complexes correlate with the total electronic charge density on the carbonyl oxygen indicating that the complexation site is carbonyl oxygen. TCE contains electron deficient carbon atoms due to the presence of electron withdrawing chlorine atoms. It can form charge transfer complexes with donor molecules [12]. In this article we present the ultrasonic velocity, density, and viscosity values of the solutions containing equimolar amounts of four cyclicketones with TCE in *n*-hexane at five different temperatures. The ultrasonic velocity, density, and viscosity values of these solutions at 303 K are given in Table I at different concentrations. The ultrasonic velocity decreases with increase in concentration even at very dilute solution, indicating the presence of strong intermolecular attraction between the cyclicketones and TCE. Figure 1 contains the plots of ultrasonic velocity *versus* concentration for a four samples. It may be noted that the ultrasonic velocity reaches minimum at a particular concentration, characteristic of cyclicketones. Out of four ketones, the decrease in ultrasonic velocity is more in the case of cyclooctanone and cyclohexanone and less in the case of the other two cyclicketones. This suggests that the molecular interactions are the strongest in cyclooctanone and weakest in cyclohexanone. At higher concentration the ultrasonic velocity value increases slightly. These observations strongly suggest that the extend of complexation is maximum at a particular concentration, characteristic of cyclicketones.

The viscosity values are plotted against concentration for the four systems at 303 K (Fig. 2). There in nonlinear variation in viscosity with concentration in all the four

TABLE I Ultrasonic velocity, density, and viscosity values of cyclicketones with TCE in *n*-hexane solutions at 303 K

Conc.,/* M × *10^{-5}*	*Ultrasonic velocity (U)* $\mathrm{ms^{-1}}$				*Density (ρ)* $\mathrm{kg\,m^{-3}}$				*Viscosity (η)* × *10^{-3}* $\mathrm{Ns\,m^{-2}}$			
	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$
1.0	1045.0	1045.2	1046.7	1044.8	646.8	647.5	644.4	649.4	0.283	0.296	0.308	0.311
2.5	1044.6	1044.8	1046.5	1044.2	647.8	648.7	645.6	650.6	0.283	0.290	0.302	0.305
5.0	1044.0	1044.1	1046.2	1043.2	648.6	650.4	646.8	651.7	0.277	0.291	0.296	0.298
7.5	1043.4	1043.4	1045.9	1042.4	649.7	651.6	648.5	652.8	0.277	0.285	0.290	0.292
10	1042.9	1042.8	1045.6	1041.5	651.5	652.3	649.7	654.5	0.271	0.278	0.284	0.286
25	1042.6	1044.8	1046.7	1043.5	652.6	644.7	643.4	650.5	0.272	0.288	0.294	0.298
50	1042.3	1045.4	1047.0	1043.0	653.7	645.8	644.5	651.6	0.265	0.289	0.288	0.291
75	1042.0	1045.8	1047.8	1042.6	654.5	646.7	645.4	652.7	0.259	0.283	0.289	0.285
100	1043.1	1044.1	1044.2	1041.9	644.8	648.2	647.3	653.9	0.275	0.276	0.283	0.286
500	1042.7	1043.7	1043.7	1041.2	645.6	650.3	648.7	655.4	0.269	0.277	0.283	0.280

*[ketone] = [TCE].

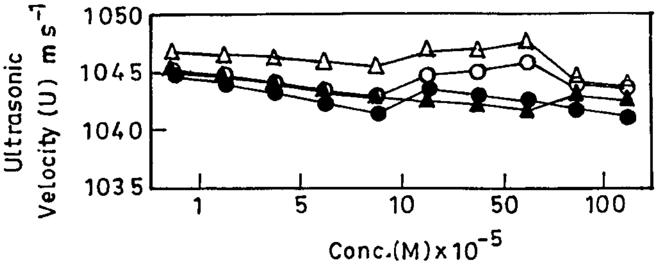

FIGURE 1 Plot of ultrasonic velocity *versus* concentration of cyclicketones with TCE in *n*-hexane solutions at 303 K.

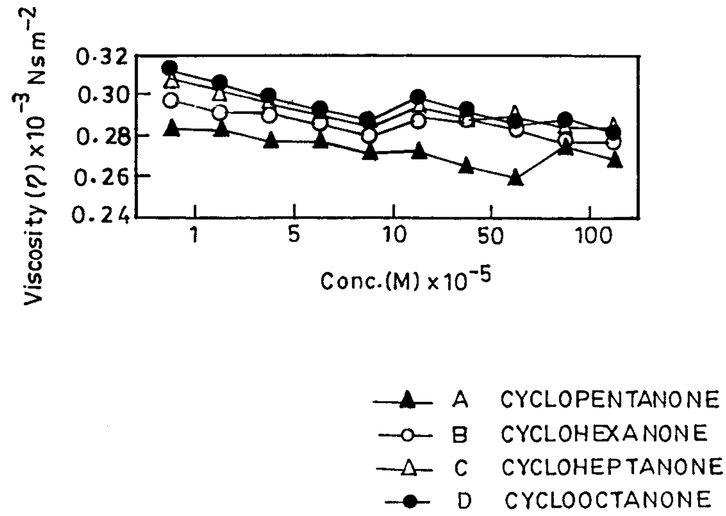

FIGURE 2 Plot of viscosity *versus* concentration of cyclicketones with TCE in *n*-hexane solutions at 303 K.

systems indicating that the charge transfer complexes are formed between the four cyclicketones and TCE. The viscosity decreases at a very low concentration, reaches minimum at a characteristic concentration and increases at moderate concentration. This behavior supports that the cyclicketones form charge transfer complexes with TCE and the complexation is maximum at characteristic concentration.

Intermolecular free length, Rao constant, and absorption coefficient values for various concentration of donor and acceptor molecules in *n*-hexane solution at 303 K calculated from ultrasonic velocity, densities are presented in Table II. The intermolecular free length is almost constant in all the four systems and independent of concentration. This suggests that there is strong intermolecular attraction even in dilute solution. However, there is a nonlinear variation in Rao constant and absorption coefficient indicating the formation of charge transfer complexes in the four systems. It may be noted that the values of intermolecular free length, Rao constant, and absorption coefficient values are almost same for the four systems at a given concentration indicating that similar complexes are formed in the four systems.

TABLE II Intermolecular free length, Rao constant, and absorption coefficient values of cyclicketones with TCE in *n*-hexane solutions at 303 K

Conc.,/* M × 10^{-5}	*Intermolecular free length* (L_f) Å				*Rao constant* (R) $\times 10^{-02}$				*Absorption coefficient* (α/f^2) $\times 10^{-15}$ $N_p m^{-1} s^2$			
	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$
1.0	0.740	0.740	0.740	0.740	0.135	0.134	0.135	0.134	10.1	10.5	11.0	11.0
2.5	0.740	0.739	0.740	0.739	0.134	0.134	0.135	0.134	10.1	10.3	10.7	10.8
5.0	0.740	0.739	0.739	0.739	0.134	0.134	0.135	0.134	9.8	10.3	10.5	10.6
7.5	0.740	0.739	0.739	0.739	0.134	0.134	0.135	0.134	9.8	10.1	10.3	10.4
10	0.739	0.739	0.738	0.739	0.134	0.134	0.135	0.134	9.6	9.8	10.1	10.2
25	0.739	0.742	0.741	0.742	0.135	0.137	0.138	0.136	9.6	10.3	10.5	10.6
50	0.738	0.740	0.740	0.740	0.137	0.138	0.140	0.139	9.4	10.3	10.2	10.3
75	0.738	0.740	0.739	0.740	0.138	0.140	0.142	0.141	9.2	10.1	10.2	10.1
100	0.743	0.740	0.740	0.740	0.142	0.141	0.144	0.143	9.8	9.8	10.1	10.2
500	0.743	0.739	0.740	0.739	0.161	0.161	0.172	0.174	9.6	9.8	10.1	9.9

TABLE III Free energy of activation, free volume, and cohesive energy values of cyclicketones with TCE in *n*-hexane solutions at 303 K

Conc.,/* M × 10^{-5}	*Free energy of activation* (ΔG^*) kJ				*Free volume* (V_f) cm^3 $(\times 10^{-7})$				*Cohesive energy* (CE) kJ			
	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$
1.0	3.36	3.42	3.35	3.28	6.42	6.00	5.67	5.57	29.99	30.62	31.31	31.34
2.5	3.36	3.36	3.36	3.28	6.42	6.19	5.84	5.74	29.97	30.32	30.88	31.05
5.0	3.29	3.37	3.28	3.22	6.64	6.17	6.04	5.96	29.58	30.29	30.62	30.67
7.5	3.29	3.30	3.22	3.22	6.65	6.37	6.24	6.15	29.57	30.01	30.20	30.28
10	3.23	3.24	3.15	3.16	6.88	6.62	6.46	6.36	29.26	29.62	29.93	29.99
25	3.24	3.26	3.09	3.10	6.92	6.38	6.24	6.10	29.19	30.23	30.43	30.54
50	3.16	3.19	3.22	3.02	7.34	6.48	6.61	6.50	28.84	30.17	30.07	30.11
75	3.10	3.36	3.22	3.22	7.74	6.82	6.75	6.89	28.35	29.68	29.98	29.64
100	3.30	3.29	3.16	3.16	7.21	7.19	7.10	7.03	29.26	29.26	29.65	29.67
500	3.24	3.24	3.10	3.09	9.05	8.77	9.28	9.73	28.31	28.63	28.76	28.45

Cohesive energy in liquid mixture is a measure of the molecular interaction between the components. Cohesive energy values along with free volume and free energy of activation (ΔG^*) are given in Table III. These values are computed from the measured ultrasonic velocity and viscosity at 303 K. The decrease in cohesive energy with increase in concentration in all the four system shows the presence of strong intermolecular attraction between the donor and acceptor molecules. This is further supported by slight increase in free volume at 303 K. The free energy of activation in an intrinsic property of the species present in the liquid mixtures. Almost constant free energies of activation values are observed in all the four systems indicating the formation of similar charge transfer complexes in these systems.

The internal pressure at various concentrations of cyclicketones and TCE in *n*-hexane solutions at 303 K are calculated from the ultrasonic velocity. Figure 3 contains the plots of internal pressure against concentration of four systems. The internal pressure decreases with increase in concentration of donor and acceptor. This suggests that the molecular interaction between the cyclicketones and TCE increases with increase in the concentration and the interactions are maximum at characteristic concentration. The variation in internal pressure with concentration at the experimental

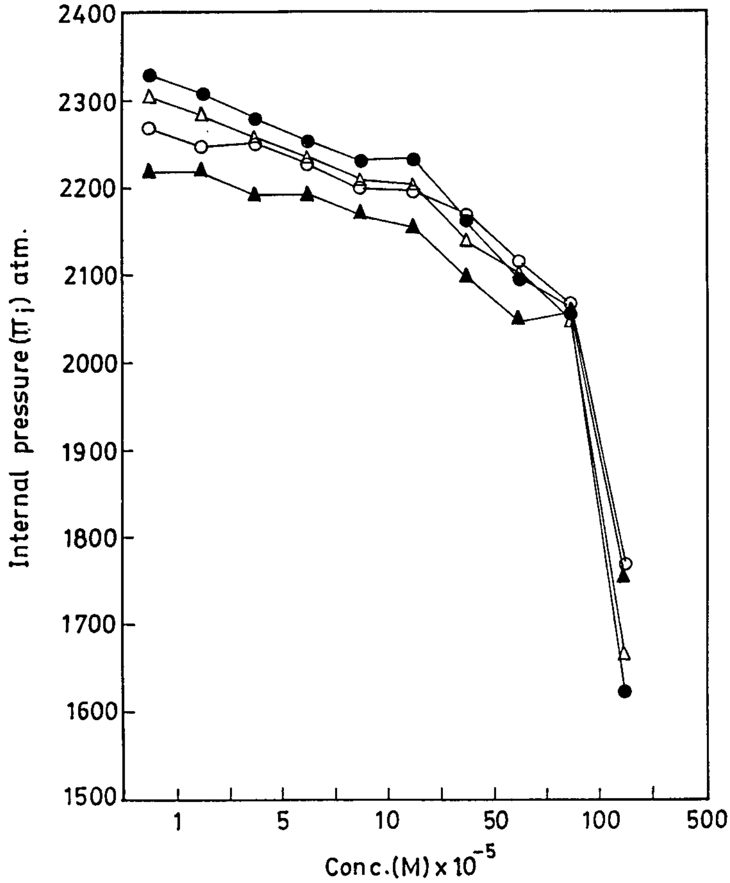

FIGURE 3 Plot of internal pressure *versus* concentration of cyclicketones with TCE in *n*-hexane solutions at 303 K.

temperature confirms the formation of charge transfer complexes between carbonyl compounds and TCE.

Molecular interaction parameters are indicative of the extent of deviation from the ideal behavior. They can be used to assess the strength of intermolecular attraction between the components of the liquid mixture. In the present investigation, molecular interaction parameters are calculated as a function of ultrasonic velocity (X_u), density (X_ρ) and viscosity (X_η). The molecular interaction parameter varies with the concentration. Table IV contains these values at 303 K for the four systems. The data in Table IV indicate that the X_u values are negative in dilute solution but positive at higher concentration for all the four systems investigated. This trend in X_u is an evidence for the formation of donor–acceptor complexes between TCE (acceptor) and cyclic ketones (donor). This is further supported by the negative values of X_ρ and X_η for all the four systems investigated.

In order to analyse the change in the cohesive forces with concentration in the four systems, cohesive energy values are plotted as a function of interaction parameter with respect to ultrasonic velocity at the corresponding concentration (Fig. 4). These plots indicate that the cohesive energy decreases as the molecular interaction increases.

TABLE IV Molecular interaction parameters with respect to velocity, density, and viscosity for cyclicketones with TCE in *n*-hexane solutions at 303 K

Conc.,/* M × *10*$^{-5}$	*Interaction parameter with respect to velocity* (X_u)				*Interaction parameter with respect to density* (X_ρ)				*Interaction parameter with respect to viscosity* (X_η)			
	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$	C_5H_8O	$C_6H_{10}O$	$C_7H_{12}O$	$C_8H_{14}O$
1.0	–0.0057	–0.0053	–0.0025	–0.0061	–0.021	–0.018	–0.028	–0.013	–0.1843	–0.1076	–0.0338	–0.0149
2.5	–0.0063	–0.0059	–0.0027	–0.0071	–0.027	–0.024	–0.033	–0.018	–0.1939	–0.1536	–0.0821	–0.0637
5.0	–0.0070	–0.0069	–0.0029	–0.0086	–0.042	–0.037	–0.048	–0.033	–0.2457	–0.1675	–0.1386	–0.1270
7.5	–0.0079	–0.0079	–0.0031	–0.0098	–0.054	–0.049	–0.058	–0.045	–0.2604	–0.2170	–0.1893	–0.1781
10	–0.0085	–0.0087	–0.0034	–0.0112	–0.064	–0.061	–0.069	–0.055	–0.3056	–0.2693	–0.2374	–0.2267
25	–0.0071	–0.0029	–0.0050	–0.0054	–0.144	–0.164	–0.168	–0.149	–0.3763	–0.3008	–0.2714	–0.2514
50	–0.0046	0.0012	–0.0010	–0.0033	–0.248	–0.266	–0.269	–0.253	–0.4969	–0.4017	–0.4058	–0.3934
75	–0.0024	0.0048	0.0029	–0.0012	–0.329	–0.345	–0.348	–0.333	–0.5825	–0.5016	–0.4802	–0.4946
100	0.0022	0.0041	0.0043	-5E-05	–0.411	–0.405	–0.406	–0.394	–0.5824	–0.5794	–0.5578	–0.5484
500	0.0265	0.0284	0.0284	0.0235	–0.725	–0.721	–0.722	–0.716	–0.8342	–0.8242	–0.8165	–0.8204

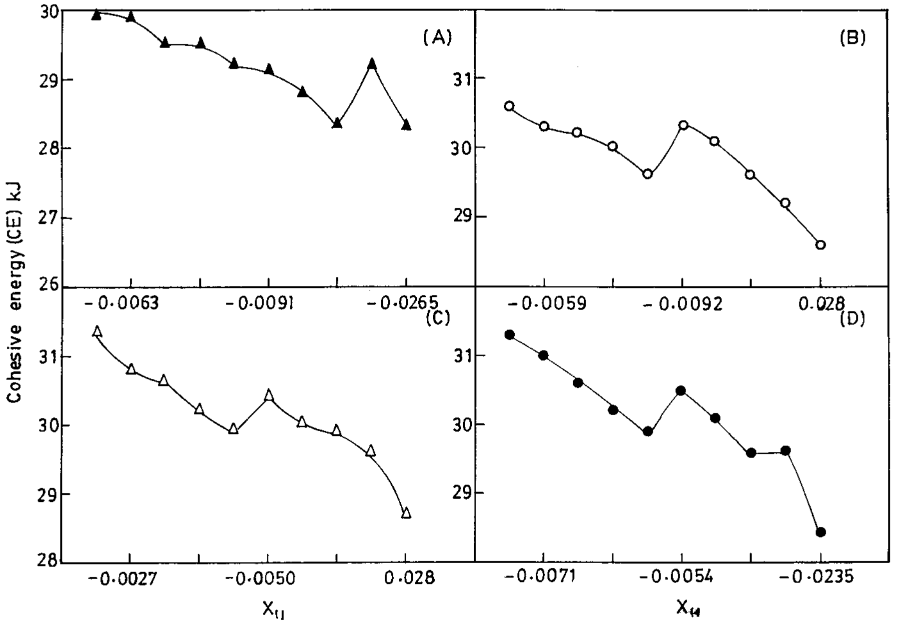

FIGURE 4 Plot of cohesive energy *versus* molecular interaction parameter (X_u) of cyclicketones with TCE in *n*-hexane solutions at 303 K.

Further, decrease in cohesive energy with increase in the molecular interaction parameter suggests that the extent of complexation increases with increase in concentration. It may be noted similar plots are obtained when X_ρ (Fig. 5) and X_η (Fig. 6) values are plotted against cohesive energy. These findings indicate that the TCE molecules are strongly attracted by the cyclicketones molecules through dipolar interactions resulting in the formation of donor–acceptor complexes.

The stability constant values of donor–acceptor complexes between cyclicketones and TCE are given in Table V. These constants are calculated from the measured ultrasonic velocities using modified Bhat equation [2]. It may be noted that the formation constants are almost constant for a given system at given temperature, indicating

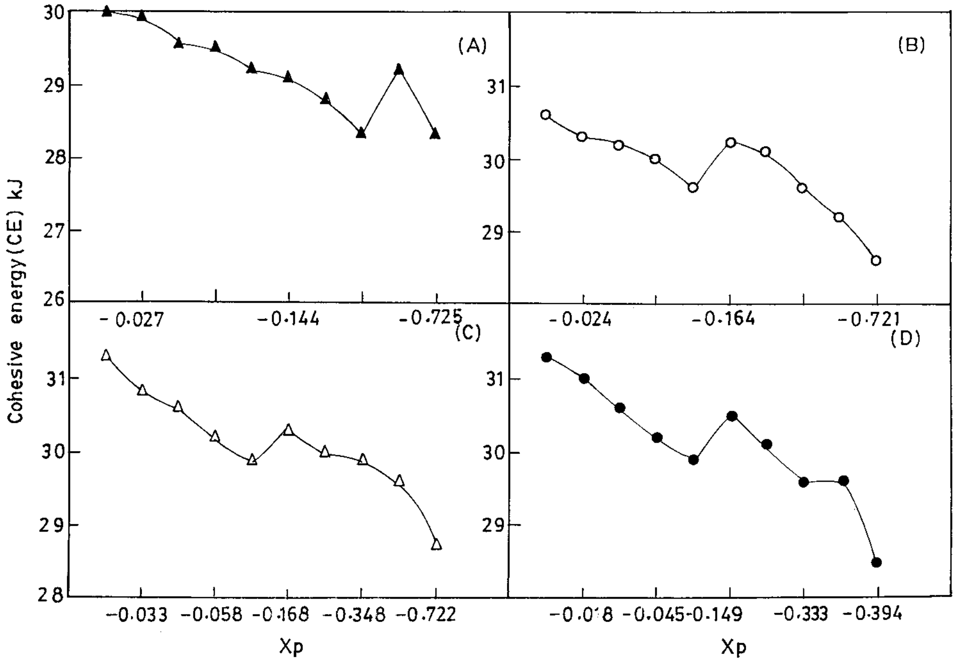

FIGURE 5 Plot of cohesive energy *versus* molecular interaction parameter (X_ρ) of cyclicketones with TCE in *n*-hexane solutions at 303 K.

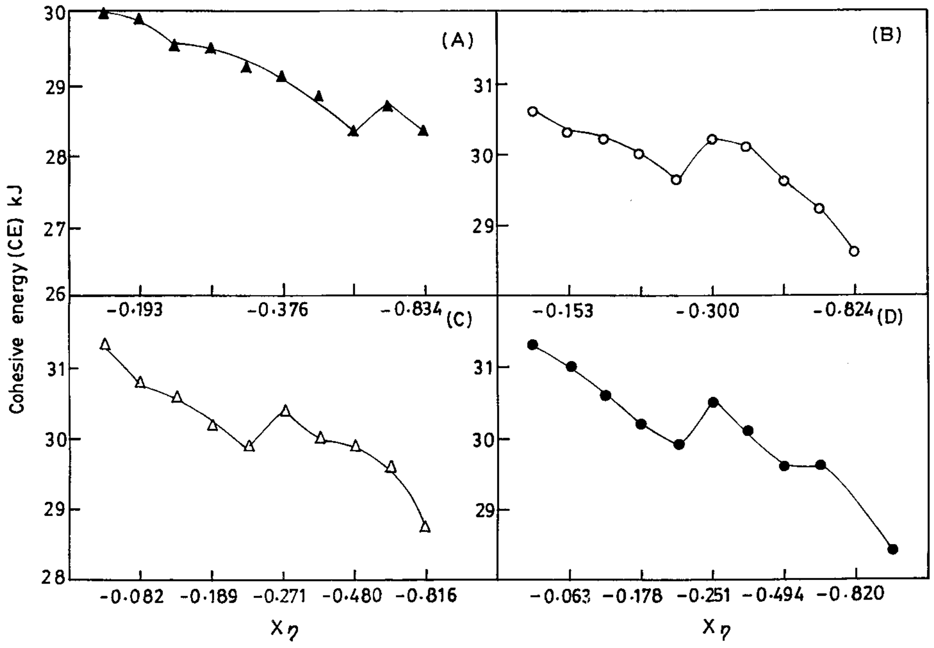

FIGURE 6 Plot of cohesive energy *versus* molecular interaction parameter (X_η) of cyclicketones with TCE in *n*-hexane solutions at 303 K.

TABLE V Formation constants of charge transfer complexes between cyclicketones with tetrachloroethylene in *n*-hexane solutions

	Conc., (M)		$293\,\mathrm{K} \times 10^3$	$298\,\mathrm{K} \times 10^3$	$303\,\mathrm{K} \times 10^3$	$308\,\mathrm{K} \times 10^3$	$313\,\mathrm{K} \times 10^3$
	$a \times 10^{-5}$	$b \times 10^{-5}$					
C_5H_8O	1.0	2.5	2.55	2.57	3.73	3.72	4.63
	2.5	5.0	2.54	2.64	2.99	4.27	3.85
	5.0	7.5	2.19	3.12	3.54	3.89	4.28
	1.0	5.0	2.54	2.61	3.31	4.01	4.20
$C_6H_{10}O$	1.0	5.0	2.97	3.64	4.18	4.83	5.86
	2.5	7.5	2.67	3.69	4.65	5.24	5.89
	1.0	7.5	2.83	3.31	4.44	5.22	5.98
	2.5	10.0	2.67	3.88	4.43	5.29	6.11
	1.0	10.0	2.79	3.51	4.32	5.26	6.13
$C_7H_{12}O$	1.0	2.5	1.17	2.03	2.71	2.89	3.91
	5.0	7.5	1.17	1.78	2.38	2.65	3.44
	1.0	5.0	1.31	1.76	2.02	3.00	3.44
	1.0	7.5	1.45	1.76	2.10	2.89	3.44
	2.5	10.0	1.43	1.63	2.01	2.87	3.58
	1.0	10.0	1.38	1.72	2.17	2.88	3.67
$C_8H_{14}O$	1.0	2.5	4.12	4.60	6.29	6.65	7.34
	5.0	7.5	4.50	5.39	4.76	6.48	7.17
	1.0	5.0	4.32	5.07	6.42	7.19	8.21
	2.5	7.5	4.50	5.41	5.77	7.23	8.35
	1.0	7.5	4.37	5.13	5.96	7.01	7.96

that the equilibrium constant (K) value depends on the structure of the cyclicketones. From the values of equilibrium constant, it is found that the stability of the charge transfer complexes formed between cyclicketones and TCE is in the order:

$$\text{cyclooctanone} > \text{cyclohexanone} > \text{cyclopentanone} > \text{cycloheptanone}.$$

The stability constants obtained are five different temperatures for the four systems are used to calculate the thermodynamic parameters for the formation of charge transfer complexes. The enthalpy change values are calculated from the slops in $\ln K$ *versus* $1/T$ (Fig. 7). It is found that the ΔH values are negative for all the four system and hence the formation of charge transfer complexes between the cyclicketones and TCE is exothermic. The thermodynamic parameters for the complexes are given in Table VI. The ΔG values are negative for all four systems indicating that the charge transfer complexes are thermodynamically stable. The formation of charge transfer complexes between cyclicketones and TCE is also supported by the negative ΔS values of the complexes. The large negative entropy change values for the four systems may be due to the combined effect of complexation and solvation of the complexes. The acoustical studies made on the four systems decisively confirm the formation of charge transfer complexes between the carbonyl compounds and TCE. The complexation may be through dipolar interaction and polarisation of the carbonyl group by the acceptor molecule. This is supported by a correlation of the stability constant (K) of the charge transfer complexes and the two molecular parameters namely polarisability and first ionization potential of the carbonyl compounds. These molecular parameters are obtained theoretically for the four cyclicketones by carrying out semiempirical molecular orbital calculations at the

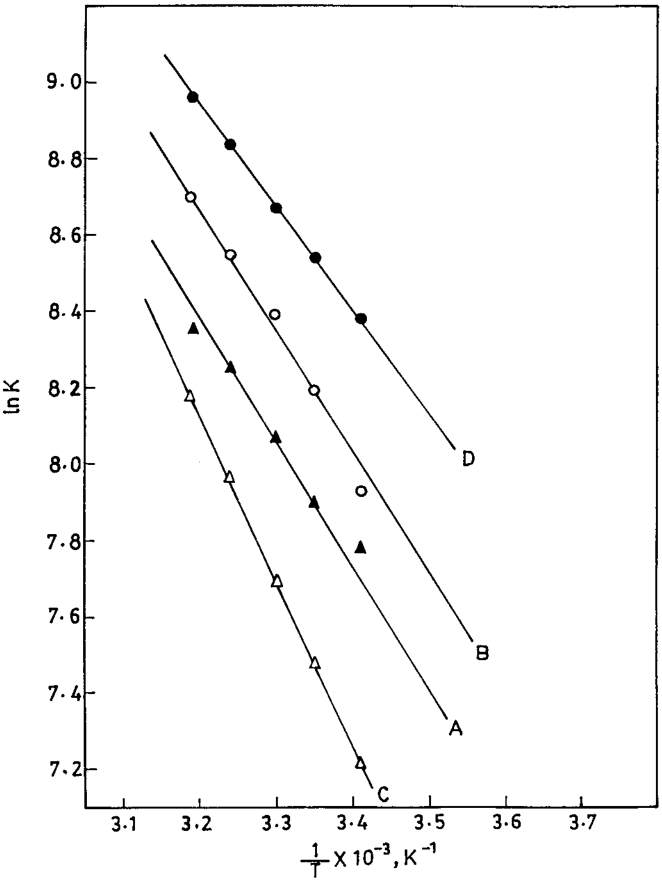

FIGURE 7 Plot of ln$K$ *versus* $1/T$ of cyclicketones with TCE in n-hexane solutions.

TABLE VI Free energy change, enthalpy change, and entropy change for the formation of charge transfer complexes between cyclicketones and TCE in n-hexane solutions

Cyclic ketone	ΔG *at 303* K (kJ mol^{-1})	ΔS *at 303* K (JK^{-1} mol^{-1})	ΔH (kJ mol^{-1})
C_5H_8O	−20.3	−145	−24.0
$C_6H_{10}O$	−21.1	−151	−24.5
$C_7H_{12}O$	−19.3	−164	−30.3
$C_8H_{14}O$	−21.9	−139	−20.2

PM3 level [2]. Figure 8a contains the plot of log$K$ *versus* polarisability. It is linear, indicating that the formation constant is directly related to the polarisability of the carbonyl compounds. Figure 8b contains the plot of log$K$ *versus* first ionization potential of the cyclicketones. It is linear but has negative slop. These findings suggest that the charge transfer complexes are formed between the four cyclicketones (donor) and TCE (acceptor) due to dipole–dipole attraction and subsequent polarisation of ketone molecules. That is why the formation constant increases with increase in the first ionization potential.

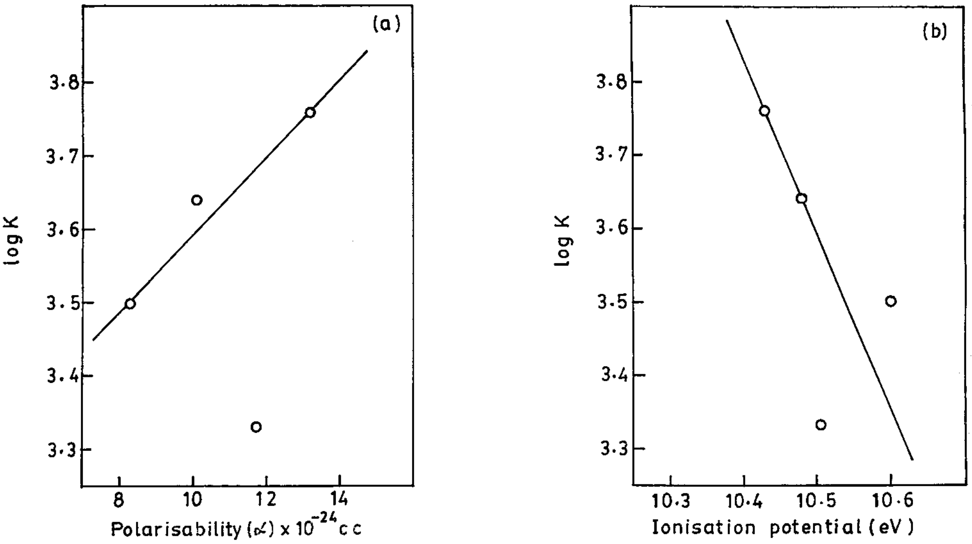

FIGURE 8 Plot of log *K* *versus* (a) polarisability and (b) ionization potential of cyclicketones.

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